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REMARKS

The amendment to the specification at paragraph [0071] is offered in order to correct inadvertent typographical and/or editorial errors. A declaration in support of the amendment, including an explanation of the nature of the errors and the basis for the amendment, is enclosed herewith. Entry of the amendment is respectfully requested.

If there are any additional charges in connection with this requested amendment, the Examiner is authorized to charge Deposit Account No. 12-1095 therefor.

Dated: May 11, 2004

Respectfully submitted,

By 

Harvey L. Cohen

Registration No.: 28,365

LERNER, DAVID, LITTENBERG,

KRUMHOLZ & MENTLIK, LLP

600 South Avenue West

Westfield, New Jersey 07090

(908) 654-5000

Attorney for Applicant

LD-447\

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Docket No.: W9652-001
(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:
Darryl P. Klein

Application No.: 10/719,551

Group Art Unit: 1754

Filed: November 20, 2003

Examiner:

For: HYDROCONVERSION CATALYSTS AND
METHODS OF MAKING AND USING SAME

DECLARATION PURSUANT TO 37 C.F.R. § 1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

I, Darryl P. Klein, do declare as follows:

1. I am a Senior Development Associate for Advanced Refining Technologies, a joint venture company of Chevron Products Company and W.R. Grace & Co.'s Davison Catalysts business unit. Since 1999 I have been involved in the development of heterogeneous catalysts for resid upgrading. I received a Ph.D. in Inorganic Chemistry with emphasis in organometallic synthesis from the University of California, Berkeley. I am an inventor or co-inventor on 18 patents and pending patent applications and I have authored or co-authored 12 publications.

2. I am the inventor of the subject patent application and participated in its preparation for filing in the United States Patent and Trademark Office. In particular, I am familiar with that portion of the application in which the catalyst characterizing feature, "Active Site Index" (ASI), is described at paragraphs [0070] and [0071]. As stated in paragraph [0070] the test method is "based on the work by *N.Y. Topsoe and H. Topsoe*, J. Catalysis (1983), 84(2), 386-401." A copy of this reference is attached for convenience.

3. The specific procedure for measuring and calculating ASI is set forth in paragraph [0071] wherein it is stated, "The Active Site Index (ASI) is calculated by dividing the

height of the peak at about 1716 cm^{-1} (believed to correspond to the promoted molybdenum sites) by the height of the peak at about 1802 cm^{-1} (believed to correspond to the unpromoted molybdenum sites)."

4. Shortly after the subject patent application was filed in the United States Patent and Trademark Office I became aware that the calculation method as described in paragraph [0071] and quoted immediately above was incorrect, although the values reported in the patent application at paragraph [101] were correctly calculated. In particular, two inadvertent errors were included in the description of the calculation method, as follows:

- (1) a typographical error was made with regard to one of the wavenumbers; specifically, the wavenumber at 1802 cm^{-1} should have been stated as 1852 cm^{-1} and
- (2) the ratio of the two wavenumbers was inadvertently inverted; specifically, the instructions in paragraph [0071] should have stated that the ratio is calculated by "dividing the height of the peak at about 1852 cm^{-1} by the height of the peak at about 1716 cm^{-1} ."

5. As support for my statement that these errors were inadvertent and typographical or editorial in nature, reference can be made to the *Topsoe and Topsoe* journal article cited above. In this article the authors identify peaks that correspond to unpromoted and promoted catalyst sites. The authors state that a promoted site can be present at about 1840 cm^{-1} and about 1850 cm^{-1} , depending on the catalyst components used, but no reference is made to a peak at about 1802 cm^{-1} . Furthermore, the ratio can only be calculated by "dividing the height of the peak at about 1852 cm^{-1} by the height of the peak at about 1716 cm^{-1} ," as stated immediately above, since this corresponds to the ratio of "promoted" to "unpromoted" sites, characterizing terms used in both the reference article and in the present application (in both paragraphs [0070] and [0071]), and, furthermore, the values reported in paragraph [101] could not have been obtained otherwise.

6. As still further support for the statements made herein, attached to this declaration are copies of the infrared scans actually used to calculate the ASI values reported in the patent application. Referring to these figures, the peaks used to calculate the ASI values are identified. The peaks correspond to the amendment submitted with this declaration in order to effect the corrections described above.

6. In conclusion, it is my opinion that persons skilled in the art, after reading *N.Y. Topsoe and H. Topsoe, J. Catalysis* (1983), 84(2), 386-401, and the above-identified patent

application at paragraphs [0071] and [101] would have learned that the value for the wavenumber recited in the application corresponding to supported sites must have been in error and that the ratio would necessarily have to be calculated as described in this declaration and in the accompanying amendment to the patent application.

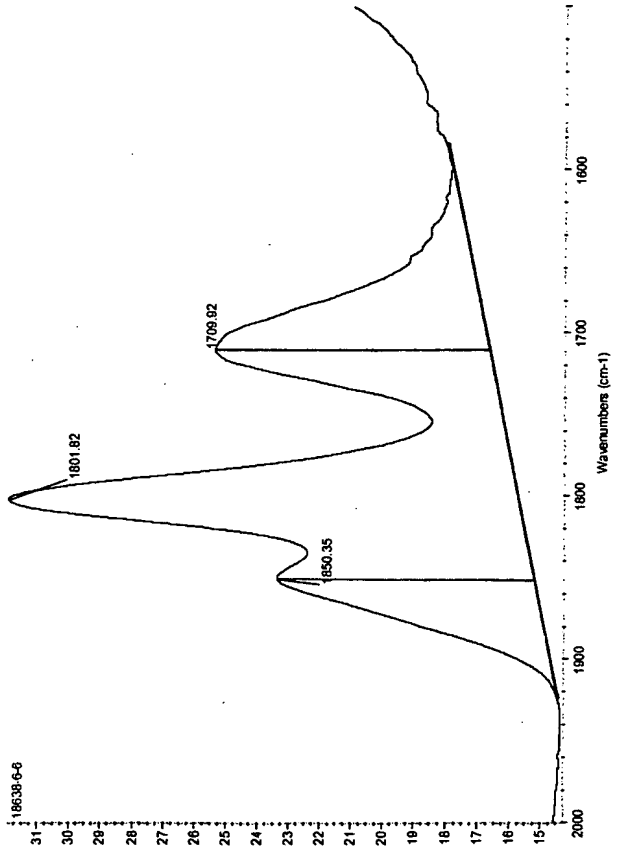
I declare under penalty of perjury that the foregoing is true and correct. I further state that I have been warned that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and such willful false statements may jeopardize the validity of the application or any patent resulting therefrom. I state that all statements made of my own knowledge are true and all statements made on information and belief are believed to be true.

Dated: May 10, 2004


DARRYL P. KLEIN

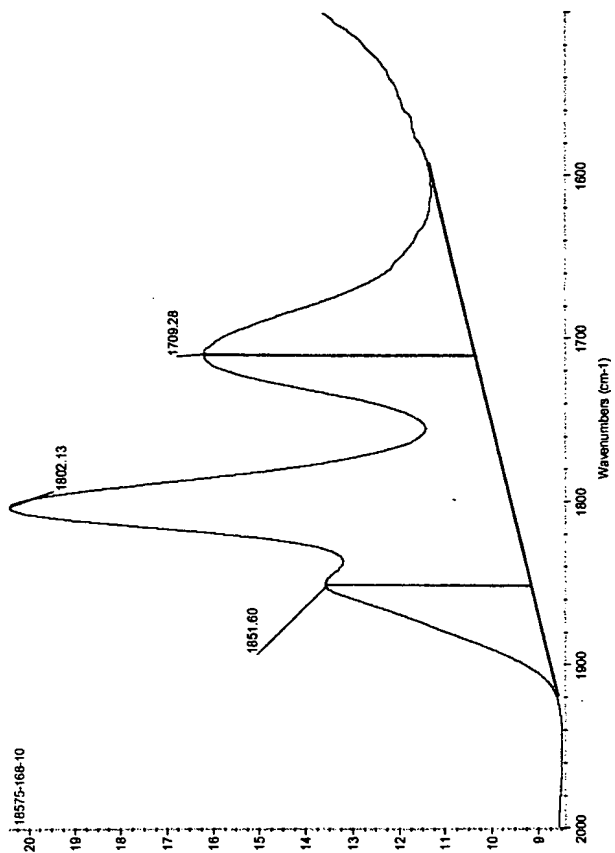


Catalyst Example 1



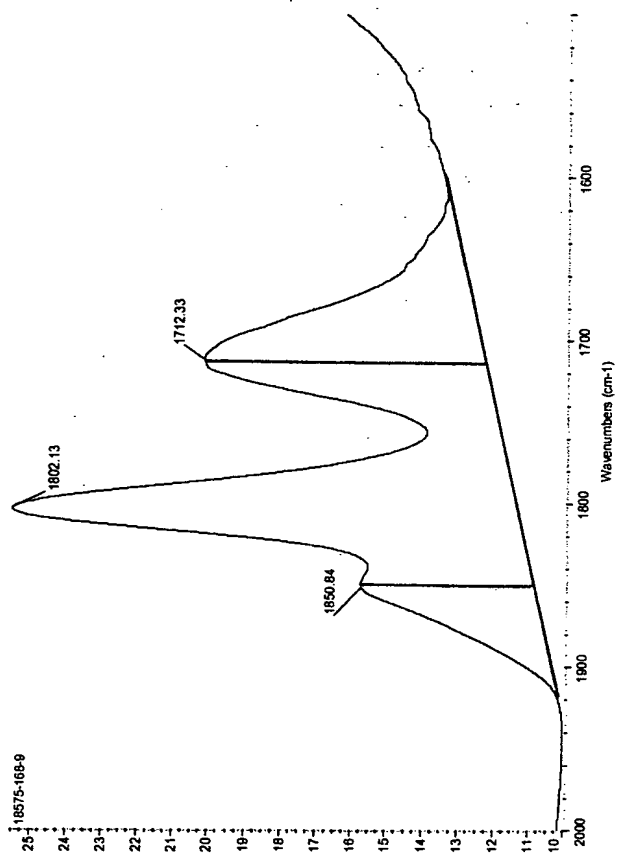


Catalyst Example 2





Catalyst Example 3 (Comparative)



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Characterization of the Structures and Active Sites in Sulfided Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ Catalysts by NO Chemisorption

NAN-YU TOPSØE AND HENRIK TOPSØE

Haldor Topsøe Research Laboratories, DK-2800 Lyngby, Denmark

Received March 15, 1983; revised June 21, 1983

Infrared and volumetric studies of NO adsorption have been used to elucidate the type of surface structures present in sulfided Co/Al₂O₃, Ni/Al₂O₃, Mo/Al₂O₃, Co-Mo/Al₂O₃, and Ni-Mo/Al₂O₃ catalysts. Catalytic implications were obtained from measurements of thiophene hydrosulfurization (HDS) activities. The content of active material in the catalysts and calcination temperature were varied in these studies. The IR bands were observed to be very different for NO adsorbed on Co, Ni, and Mo atoms and are sensitive to the surface concentration of the element, the nature of the surface phase and the extent of sulfiding or reduction. For Mo/Al₂O₃ catalysts, the NO most probably adsorbs on edge or corner sites of MoS₂-like structures and the adsorption therefore reflects the edge dispersion of these structures. In the case of the promoted Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts, the IR studies give simultaneous information on the NO adsorption occurring on the Co or Ni promoter atoms and that occurring on the Mo atoms. It is seen that the addition of promoter atoms results in a decreased adsorption on the Mo atoms. This indicates that the promoter atoms occupy edge positions of the MoS₂ "support". The Co atoms located in such positions are found to be related to those present in the so-called Co-Mo-S structure identified previously by Mössbauer emission spectroscopy. Evidence for similar Ni-Mo-S type structures is found. The HDS activity correlated neither with the total amount of chemisorbed NO nor with the amount of NO adsorbed on the Mo atoms. However, for all the catalysts a good correlation was observed between the HDS activity and the amount of NO adsorbed on the Co or Ni promoter atoms. This further supports the "Co-Mo-S model" in which the primary role of the promoter atoms is to create new sites (associated with the promoter atoms) with higher intrinsic HDS activity than that of the unpromoted sites. Pyridine, which is known to be a partial HDS poison, was observed to block a large fraction of the NO adsorption sites.

1. INTRODUCTION

Probe molecules have in recent years been used extensively to provide insight into the nature of the active sites in hydrodesulfurization (HDS) catalysts. For unpromoted MoS₂ catalysts, oxygen chemisorption correlates well with the HDS activity (1). Recently (2), this has also been observed to be the case for alumina-supported Mo catalysts and for such catalysts, CO adsorption correlated with the activity as well.

Co-Mo and Ni-Mo catalysts have also been studied by chemisorption methods. However, for these promoted systems the adsorption behavior seems much more complex than for the unpromoted catalysts.

In the case of oxygen chemisorption, some authors have found indications for correlations with the activity (3-5) while others have reported results which show that no simple relations exist between the catalytic activity and the oxygen chemisorption (6-9). Previous Mössbauer emission spectroscopy (10, 11) and EXAFS results (12) show that Co-Mo catalysts have Co atoms located in surface positions and that they are affected by the exposure to oxygen atoms. Consequently, adsorption studies of promoted catalysts may be complicated by the possibility of the adsorption occurring on both Mo and Co (Ni) atoms. Recently, the HDS activity of different supported and unsupported Co-Mo catalysts was shown to be related to the amount of Co atoms

present as Co-Mo-S (13-18). In view of this it seems likely that the presence or absence of correlations between the catalytic activity and the amount of probe molecules adsorbed will be related to what extent the probe molecules have titrated the sites associated with the promoter atoms.

To elucidate further the nature of the active sites in promoted catalysts, it may therefore be useful to utilize a technique which may provide information on the sites associated with both the Co (Ni) and Mo atoms. Recently (19-21), we have shown that in the case of calcined Co-Mo/Al₂O₃ catalysts, such information may be obtained by means of infrared studies of NO adsorption. Adsorption of NO has also been used to characterize reduced Mo/Al₂O₃ catalysts (22-27) and sulfided Mo/Al₂O₃ catalysts (28, 29) but no such studies have, to our knowledge, appeared for promoted Co-Mo/Al₂O₃ or Ni-Mo/Al₂O₃ catalysts in their active sulfided state. The present paper reports NO adsorption studies of such catalysts and it is seen that qualitative and quantitative information can be obtained about both the promoter and the Mo atoms. This allows one to elucidate the nature of the active sites and the role of the promoter atoms. The results give further support for the presence of Co-Mo-S and Ni-Mo-S type structures and give new insight into the location of the promoter atoms in these structures.

II. EXPERIMENTAL

The preparation of Co/Al₂O₃ (0.26, 2.0, or 6.5% (wt) Co), Mo/Al₂O₃ (8.0% Mo), and Co-Mo/Al₂O₃ (1.8% Co and 8.4% Mo) catalysts has been given previously (19). In short, these were prepared by depositing the active materials onto η -Al₂O₃ (surface area, 230 m²g⁻¹) via impregnation or coimpregnation in the case of the Co-Mo/Al₂O₃ catalyst, followed by drying and calcining at 773 K in air for 2 h. Besides the above coimpregnated Co-Mo/Al₂O₃ catalyst, a series of sequentially impregnated Co-Mo/Al₂O₃ catalysts with different Co/Mo ratios

was prepared as described in Ref. (13) by adding appropriate amounts of Co in the form of cobalt nitrate to a batch of calcined Mo/Al₂O₃ catalyst (8.6% Mo impregnated on another η -Al₂O₃ with surface area of 250 m²g⁻¹) by the incipient wetness impregnation method. The catalysts were then dried and calcined as described above.

The Ni/Al₂O₃ (0.57 and 5.76% Ni) and Ni-Mo/Al₂O₃ catalysts (Ni/Mo atomic ratio = 0.09, 0.27, 0.53, 0.75, and 1.2) were prepared analogously except for the fact that aqueous solutions of nickel nitrate were used.

Unless otherwise stated, sulfidation was carried out *in situ* by passing a gas mixture consisting of approx. 1.7% H₂S in H₂ over the calcined precursors at 673 K for 2 h. Shorter and longer sulfiding times were also studied. The results varied quantitatively, but since similar relative changes between the different catalysts were observed, only the results for 2 h sulfiding will be reported. Following the sulfidation, the H₂S gas mixture and chemisorbed H₂S were removed by flushing the cell with purified N₂ at the same temperature for 16 h. After treatment in N₂, the samples were slowly cooled to ambient temperature in the N₂ flow and evacuated to 10⁻⁵ Torr. It was found that besides the preparation procedure and the type of Al₂O₃ employed, the pretreatment conditions were also very important and different results were obtained with just small changes in the conditions such as the temperature and time of N₂ flushing. Thus, great care was taken to keep the preparation procedure and pretreatment conditions constant in all cases where quantitative comparisons were made.

Nitrogen was purified by passage through Cu turnings at 523 K and a molecular sieve trap (Linde 5A) kept at 195 K. Nitric oxide, 99% (AGA A/S) was purified by freeze-thaw cycles as described in Ref. (30). The adsorption of NO was in all cases carried out at ambient temperature. Pyridine (spectroscopic grade) was purified by freeze-thaw cycles. Adsorption of pyridine was

carried out at 423 K in order to measure mainly the chemisorbed species. Spectra were recorded after the excess pyridine had been removed by evacuation at 423 K. The *in situ* infrared cell and the Perkin-Elmer 180 spectrometer connected to a Nicolet signal averager have been described previously (19). Unless stated otherwise, all absorbances are given as peak heights after deconvolution.

The procedures used for volumetric measurements of NO adsorption are the same as those described in detail earlier (19). Briefly, they were carried out at room temperature using a constant volume system equipped with a Texas Instrument precision pressure gauge. The amount of NO adsorbed was obtained by taking the difference between a first and a second isotherm (obtained after evacuation for 1 h) or by extrapolating to zero pressure. Both methods gave quite similar results but only the values calculated from the latter procedure are given here.

The thiophene HDS activity measurements were performed on the same series of catalysts as used for NO adsorption. For the Co-Mo/Al₂O₃ catalysts the procedures and some of the results have been reported previously (13).

III. RESULTS

A. Mo/Al₂O₃

Sulfidation of a calcined 8% Mo/Al₂O₃ catalyst led to pronounced changes in the NO absorption spectra (compare Figs. 1a and c). Two bands are observed as for the calcined sample but with greater intensity. At the same time, the band positions have shifted slightly downward as compared with those for reduced (Fig. 1b) or calcined (Fig. 1a) samples which show similar band frequencies (i.e., the bands shift from 1804 and 1693 cm⁻¹ for calcined or reduced samples to about 1780 and 1685 cm⁻¹ for the sulfided sample). The spectral features of the reduced catalysts, as well as the amount of NO adsorbed (NO/Mo = 0.06), are in good agreement with those of other work-

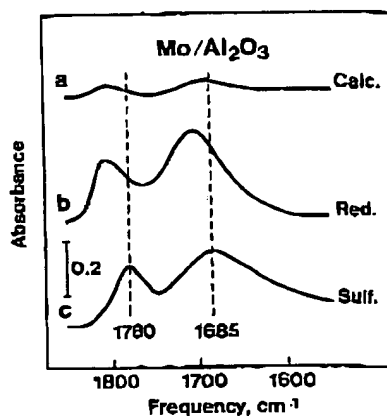


FIG. 1. Infrared spectra of NO adsorbed on an 8% Mo/Al₂O₃ catalyst after different treatments. (a) Calcination at 773 K, (b) calcination at 773 K followed by H₂ reduction at 773 K, and (c) calcination at 773 K followed by sulfidation at 653 K.

ers (see, e.g. (22)) and will not be discussed further here. Okamoto *et al.* (28) have reported quite similar frequencies for reduced Mo/Al₂O₃ catalysts and the same lowering of frequencies upon sulfiding. The downward frequency shifts are indicative of an increase in the electron density at the metal adsorption site, resulting in a stronger molybdenum-nitrogen bond and a weaker N-O bond. This is most likely due to a complete or partial replacement of oxygen ions surrounding the molybdenum atoms in the calcined state by less electronegative sulfur ions. This phenomenon is seen to be general for all the sulfided catalysts.

The intensity of the two bands varies in parallel during adsorption and desorption and thus these bands are most likely to be related to the same adsorbed NO species. As concluded for the calcined (19, 20) and reduced Mo/Al₂O₃ (22-27) catalysts, NO is most probably adsorbed mainly as a dinitrosyl (or possibly dimeric) complex. The absorption bands, especially the lower frequency band, are quite broad. This was also observed by Yao and Rothschild (25) to be the case for reduced Mo/Al₂O₃ catalysts and was related to a distribution of surface adsorption sites with different degree of co-

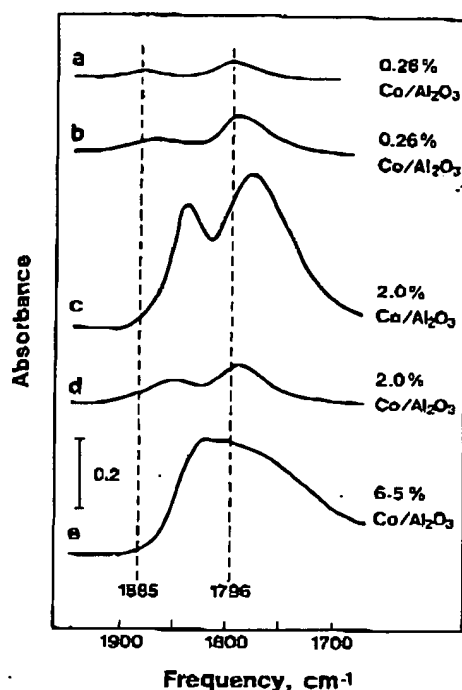


FIG. 2. The effects of loading and precalcination temperature on the ir spectra of NO adsorbed on sulfided Co/Al₂O₃ catalysts. (a) The 0.26% Co/Al₂O₃ after calcination at 773 K. (b) as (a) after sulfiding at 653 K. (c) 2% Co/Al₂O₃ calcined at 773 K followed by sulfiding at 653 K. (d) as (c) but precalcined at 923 K. (e) 6.5% Co/Al₂O₃ calcined at 773 K followed by sulfiding at 653 K.

ordinative unsaturation (CUS) and varying degrees of interaction between adjacent adsorbate molecules. Alternatively, as suggested by Howe and Kemball (31), it could be due to more than one type of adsorption complex. The broadness may also be due to contributions from adsorption on different phases (e.g., unsulfided or partially sulfided species). However, such species are probably not present to any great extent since EXAFS investigations (32) of this type of catalyst show that MoS₂-like species dominate.

In agreement with the ir results, volumetric chemisorption results also show that much more NO is adsorbed on the sulfided 8% Mo/Al₂O₃ (NO/Mo = 0.17) as compared with the adsorption on the calcined sample.

B. Co/Al₂O₃

Figure 2 shows the results of NO adsorption on Co/Al₂O₃ catalysts as a function of metal loading and prior calcination temperature. The catalysts shown in Fig. 2b-e have all been sulfided at 653 K. The 0.26% Co/Al₂O₃ catalyst shows two bands at 1868 and 1790 cm⁻¹ with the latter being the most intense. In many respects the spectrum resembles that seen before sulfidation (Fig. 2a) except for a shift of the bands of 5–15 cm⁻¹ toward lower frequency in the sulfided catalyst indicating that some sulfiding of the Co atoms has taken place (see above). Increase in the intensity of the bands is observed between the calcined and sulfided samples. Upon increasing the cobalt loading to 2% (Fig. 2c), the total absorbance increases considerably, and the two bands have shifted to even lower frequencies (1842 and 1778 cm⁻¹). Again, the intensity of the bands is seen to increase upon sulfiding. However, the amount of NO adsorbed in the calcined (NO/Co = 0.49) and sulfided state (NO/Co = 0.42) is very similar. Thus, the integral molecular absorption coefficient increases upon sulfiding (to about 1.5 × 10⁻¹⁷ cm/molecule).

A further increase in the cobalt loading to 6.5% (Fig. 2e) resulted in a marked change in the NO absorption spectrum. A poorly resolved broad band with apparent band contributions around 1815 and 1750 cm⁻¹ is now observed. The total intensity, as well as the amount of NO adsorbed, have not increased proportionally with the Co loading but are about the same as for the 2% Co/Al₂O₃ catalyst. This is shown in Fig. 3 (the total integrated absorbance is used in Fig. 3a in view of the variable band positions and the extensive band overlap in the high Co loading sample). This suggests the presence of a bulk Co phase at high Co concentration. In fact, X-ray diffraction analysis of the 6.5% Co/Al₂O₃ clearly showed the presence of Co₉S₈. The above loading variation resembles that of the calcined catalysts (19).

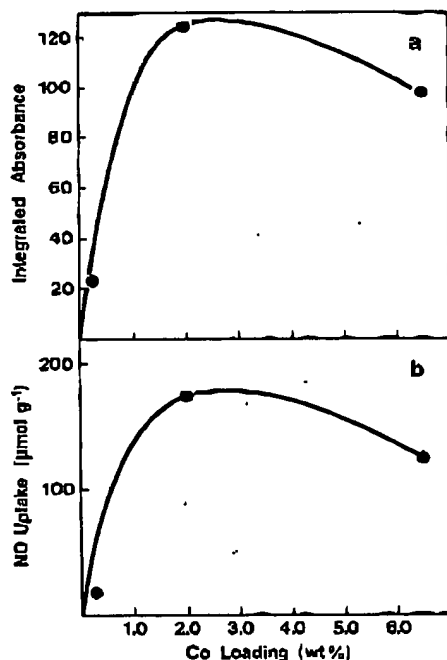


FIG. 3. The dependence of the NO adsorption on the metal loading for sulfided Co/Al₂O₃ catalysts. (a) The total integrated absorbances of the ir absorption bands and (b) the volumetric NO uptakes (all catalysts had been precalcined at 773 K).

The sulfided 2% Co/Al₂O₃ sample, which had been precalcined at a higher temperature of 923 K (Fig. 2d), showed bands which were only about one-third as intense as those observed for the same catalyst precalcined at 773 K (Fig. 2c). Furthermore, slightly higher frequencies are observed for the catalyst calcined at the higher temperature.

C. Co-Mo/Al₂O₃

The NO absorption spectrum of the sequentially impregnated Co-Mo/Al₂O₃ catalyst (Co/Mo atomic ratio = 0.44) after sulfiding is shown in Fig. 4c. Three bands at 1850, 1785, and 1690 cm⁻¹ are seen, where the highest frequency band appears as a shoulder and the lowest frequency band is quite broad. The 1785-cm⁻¹ band is the most intense band. All three bands have increased in intensity and have shifted to

lower frequencies (see Fig. 4) when compared with those in the calcined Co-Mo/Al₂O₃ catalyst (as shown by arrows in Fig. 4. See also (19)). This again implies that sulfiding of Co and Mo atoms has occurred. From a comparison with the spectra of NO adsorbed on Co/Al₂O₃ (Fig. 4b) and Mo/Al₂O₃ (Fig. 4a), it is clear that the high frequency band originates from NO adsorption on Co and the low frequency band is due to NO adsorption on Mo. The high intensity band in the center (i.e., around 1785 cm⁻¹) contains contributions from both Co and Mo, and thus only three bands are observed for the Co-Mo/Al₂O₃ catalyst.

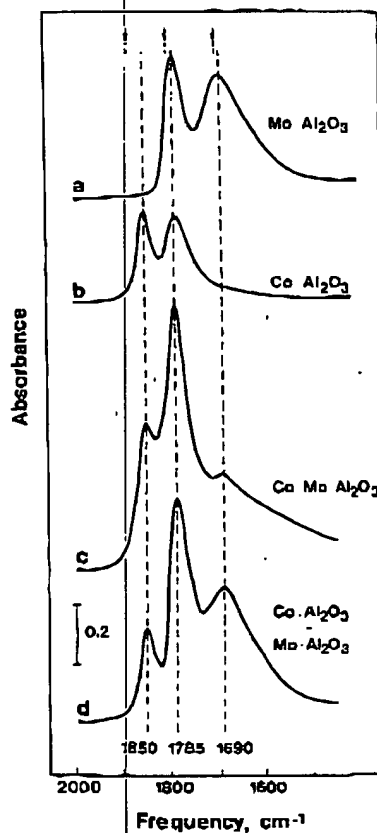


FIG. 4. Infrared spectra of NO adsorbed on sulfided catalysts: (a) 8% Mo/Al₂O₃, (b) 2% Co/Al₂O₃, and (c) Co-Mo/Al₂O₃ (Co/Mo = 0.44). Spectrum (d) is the theoretical sum spectrum of (a) and (b). Arrows show the band positions of the corresponding calcined Co-Mo/Al₂O₃ catalyst.

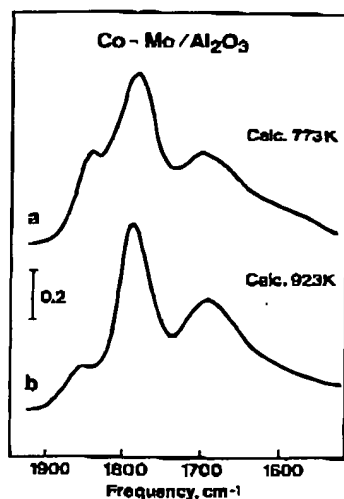


FIG. 5. The effect of calcination temperature on the ir spectra of NO adsorbed on a sulfided 1.8% Co-8.4% Mo/Al₂O₃ catalyst. (a) Calcined at 773 K. (b) Calcined at 923 K.

A computed addition spectrum (Fig. 4d) of the spectra of the Mo/Al₂O₃ and Co/Al₂O₃ catalysts with similar loadings as in the Co-Mo/Al₂O₃ catalysts shows a spectrum which has bands at about the same position as the observed spectrum (Fig. 4c). It is, however, clear that the intensity of the Mo component is lower in the spectrum of the Co-Mo/Al₂O₃ catalyst than in the sum spectrum, whereas the intensity of the Co component is higher. This behavior is more clearly demonstrated by the series of catalysts with different Co/Mo ratios discussed below.

As seen for the Co/Al₂O₃ sample, a higher precalcination temperature leads to a much lower intensity of the Co band after sulfiding (Fig. 5) and to a slight, upward frequency shift. However, at the same time the intensity of the Mo band is seen to increase. The variation of the absorbances is shown in Fig. 6a and the HDS activities of the same catalysts are shown in Fig. 6b.

The volumetric adsorption results of the series of sequentially impregnated Co-Mo/Al₂O₃ catalysts (where the Mo concentration was kept constant) are shown in Fig. 7a

as a function of Co/Mo ratios. Figure 7b shows the absorbance of the ir bands due to NO adsorbed on Co and Mo atoms (the peak heights of the highest and the lowest frequency nonoverlapping bands after deconvolution are used) versus the Co/Mo ratios. The variation in the band intensity of the Co and Mo bands shows some similarities with that observed for the catalysts calcined at different temperatures (Fig. 6a). The fraction of Co adsorbing NO is seen to increase with increasing Co/Mo, whereas at the same time the fraction of Mo adsorbing NO decreases. Further analysis of the spectra shows that besides the concentration dependence of the band intensity, the relative intensity of the bands appears to differ from that of the individual component catalysts. Although it has not been possible at this time to fully describe these differences due to the overlapping bands, the differences do seem to suggest the presence of some type of interaction between Co and Mo atoms. This may lead to changes in

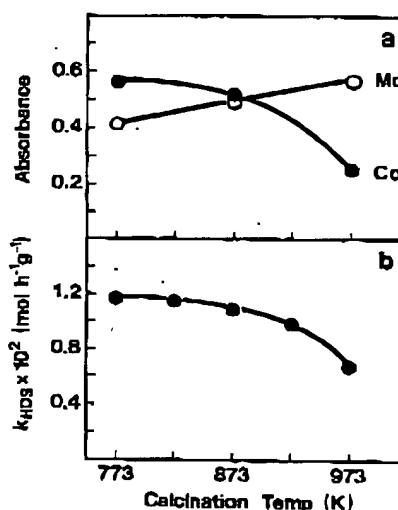


FIG. 6. The effects of calcination temperature on the NO adsorption and HDS activity for a sulfided Co-Mo/Al₂O₃ catalyst. (a) The absorbances of the ir bands of NO adsorbed on Co and Mo (peak heights at 1850 and 1690 cm⁻¹ are used, respectively) and (b) the thiophene HDS activities (activity data adapted from (17)).

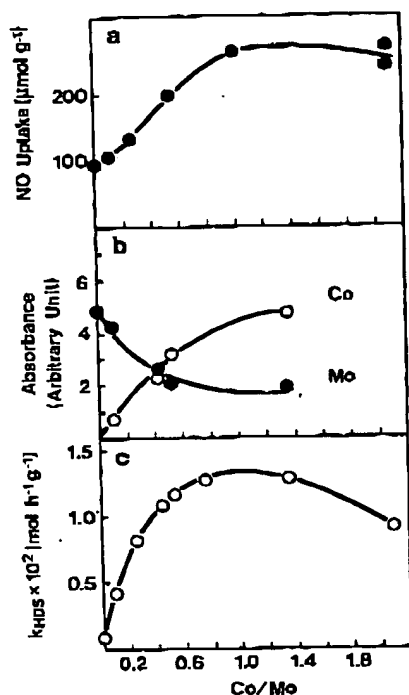


FIG. 7. The effect of Co loading (or Co/Mo ratio) on the NO adsorption and HDS activity for sulfided Co-Mo/Al₂O₃ catalysts. (a) The total volumetric NO uptakes, (b) the absorbances of the ir bands of NO adsorbed on Co and Mo (taken as peak heights of the bands at 1850 and 1690 cm⁻¹ after deconvolution, respectively), and (c) the thiophene HDS activities (activity data adapted from (13)). (The catalysts all had the same Mo loading.)

bond angle between two nitrosyl groups giving rise to the observed changes in relative band intensity (see, e.g., (19, 25)). Figure 7c shows the thiophene HDS activity (expressed as pseudo 1st order rate constants) of these catalysts (data adapted from (13)). From a comparison of Figs. 7b and c, it appears that the Co sites of the Co-Mo/Al₂O₃ catalysts titrated by NO correlate quite well with the activity. This is more clearly demonstrated in Fig. 8a, where the activities are plotted against the absorbance of the Co band. A linear correlation between HDS activity and the concentration of the titrated surface Co is seen for catalysts with Co loading up to Co/Mo

~ 0.4. At a higher Co concentration, the correlation starts to deviate from linearity. From Fig. 7 it is clear that the more active catalysts show less adsorption on sites associated with Mo, and Fig. 8b shows that no correlation exists between activity and Mo sites, in fact, a negative relationship is seen. Figures 7 and 8c show that although there is some tendency of the catalysts with high activity to adsorb more NO, no simple correlation exists between the activity and the total uptake of NO. For all the catalysts, the volumetric uptake contains contributions, as seen by ir, from NO adsorption on both Co and Mo. These contributions may not reflect the relative surface concentration of Co and Mo since

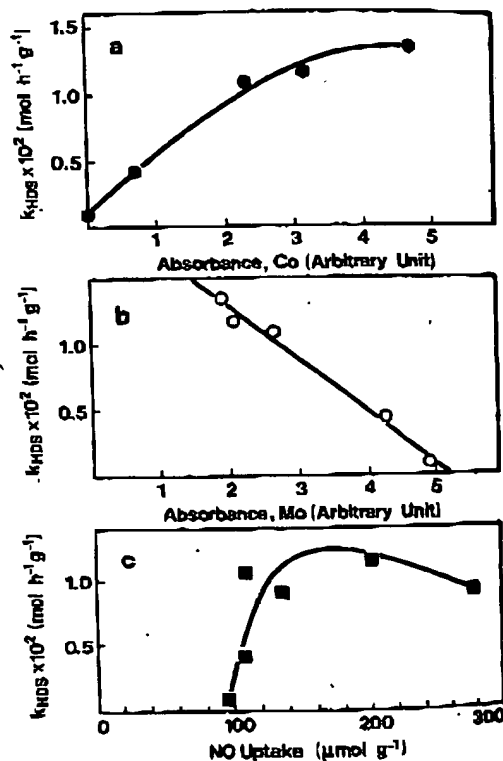


FIG. 8. The dependence of the HDS activity of sulfided Co-Mo/Al₂O₃ catalysts on different parameters. (a) The absorbances of the ir band of NO adsorbed on Co (at 1850 cm⁻¹), (b) the absorbances of the ir band of NO adsorbed on Mo (at 1690 cm⁻¹), and (c) the total volumetric NO uptakes.

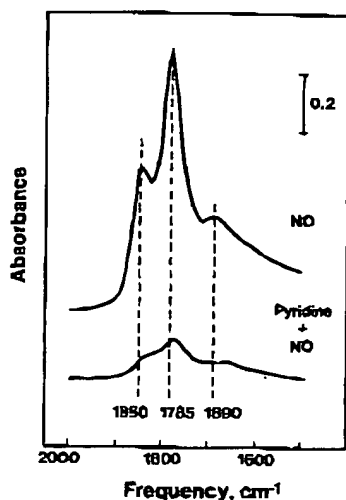


Fig. 9. The influence of preadsorption of pyridine on the ir spectra of NO adsorbed on a sulfided Co-Mo/Al₂O₃ (Co/Mo = 0.44) catalyst.

the adsorption stoichiometry may be different and may depend on experimental conditions (which may influence the degree of coordinative unsaturation (CUS)).

Pyridine has been found to partially poison sulfided Mo/Al₂O₃ (33) and Co-Mo/Al₂O₃ (34, 35) catalysts toward desulfurization of benzothiophene. In order to characterize the nature of the NO adsorption sites on the Co-Mo/Al₂O₃ catalyst further, pyridine was preadsorbed at 423 K on the surface before NO adsorption. This leads to a drastic decrease in the amount of NO adsorbed on both Co and Mo atoms, as shown in Fig. 9. The bands also shift to lower frequencies possibly due to the presence of several adsorption sites on the sample and that pyridine poisons mainly the high frequency sites. These observations are quite similar to those reported for reduced Mo/Al₂O₃ (27). According to these authors, the shift to lower frequencies is explained by the fact that the pyridine is also adsorbed on the uncovered alumina surface and this enhances the electron back-donation into the NO adsorbed on the neighboring surface metal sites.

D. Ni/Al₂O₃

Adsorption of NO on sulfided Ni/Al₂O₃ catalysts gives rise to one strong absorption band (Fig. 10b) in contrast to the Co system where two distinct bands are usually observed. This band with a frequency at 1830 cm⁻¹ is, however, slightly asymmetric toward the low frequency side and this may, as has been suggested for reduced Ni/SiO₂ catalysts (36), be due to the presence of dinitrosyl species. The band frequency for the sulfided catalysts has shifted downward as compared with the same catalysts in their calcined state, as shown in Fig. 10a (i.e., a shift from 1865 to 1830 cm⁻¹ for 0.57% Ni/Al₂O₃ and from 1848 to about 1830 cm⁻¹ for 5.76% Ni/Al₂O₃) indicating a sulfided environment as discussed above. The absorbance for both catalysts has also increased somewhat upon sulfiding. However, volumetric measurements show a slight decrease in NO uptake for the 0.57% Ni/Al₂O₃ (from NO/Ni = 0.55 to NO/Ni = 0.40) after the catalyst was sulfided, indicating an increase in the integral molecular absorption coefficient (from 1.8 × 10⁻¹⁸ to 4.0 × 10⁻¹⁸ cm/molecule).

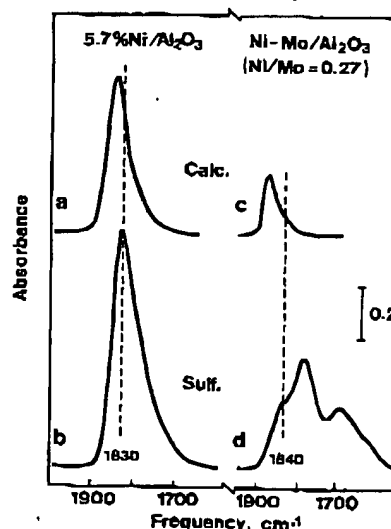


Fig. 10. Infrared spectra of NO adsorbed on calcined and sulfided Ni/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts.

E. Ni-Mo/Al₂O₃

Three absorption bands at about 1840, 1784, and 1685 cm⁻¹ are seen for the sulfided Ni-Mo/Al₂O₃ catalysts (Ni/Mo = 0.27) as shown in Fig. 10d. The corresponding calcined catalyst only shows a Ni band at 1880 cm⁻¹ (Fig. 10c) since no reduced Mo species are present (19). The bands in the sulfided catalyst are also shifted from the bands of a H₂-reduced Ni-Mo/Al₂O₃ catalyst (Ni/Mo = 1.20) which shows bands at 1860, 1800, and 1690 cm⁻¹ (a Ni band at 1876 cm⁻¹ is seen for the calcined catalyst). The highest frequency band in the sulfided catalyst is attributed to NO adsorbed on Ni, whereas the other two bands are due to NO adsorbed on Mo. The frequency of the Ni band was observed to be dependent on the Ni concentration as lower frequency is seen for catalysts with higher Ni loading. It is also evident that the frequency of the Ni band in Ni/Al₂O₃ is lower than that found for Ni-Mo/Al₂O₃. This is much more clearly seen in the calcined catalysts, where the Ni band lies at 1848 and 1865 cm⁻¹ for the low and high loading Ni/Al₂O₃ catalysts, respectively, whereas the band frequency varies from 1881 to 1876 cm⁻¹ for the Ni-Mo/Al₂O₃ catalysts with Ni/Mo ratios increasing from 0.09 to 1.20. As for the sulfided Co-Mo/Al₂O₃ catalysts, the positions of the Mo bands remain quite constant for the sulfided Ni-Mo/Al₂O₃ catalysts with different Ni/Mo ratios.

It is seen that the amount of Ni titrated by NO (Fig. 11a) increases with increasing Ni/Mo ratio (Mo is at a constant level), whereas NO adsorbed on Mo decreases. By comparison with Fig. 11c, it is seen that the HDS activity follows quite closely the NO adsorption on the Ni atoms. Figure 11b shows that there is a tendency for the more active catalysts to have a higher total uptake of NO but as in the case of the Co-Mo/Al₂O₃ catalysts, no simple correlation exists between the HDS activity and the total NO uptake. It should be mentioned that catalytic synergy is also seen for the Ni-Mo/Al₂O₃ catalysts.

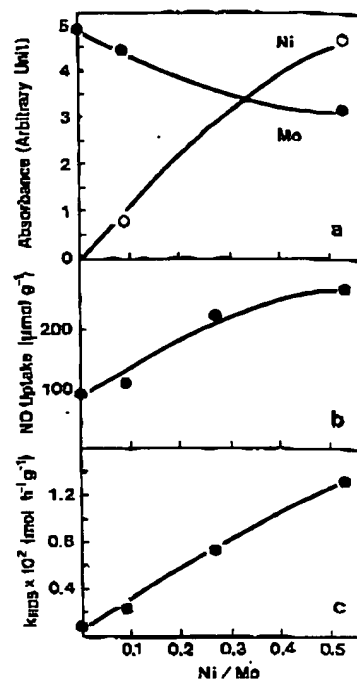


FIG. 11. The effect of Ni loading (or Ni/Mo ratio) on the NO adsorption and HDS activity of sulfided Ni-Mo/Al₂O₃ catalysts. (a) The absorbances of the IR bands of NO adsorbed on Ni and Mo (as peak heights of bands at 1835 and 1690 cm⁻¹, respectively), (b) the total volumetric NO uptakes, and (c) the thiophene HDS activities. (The catalysts all had the same Mo loading.)

IV. DISCUSSION

It is seen from the present results that NO is a useful probe molecule for the characterization of sulfided Co, Ni, and Mo catalysts. For each type of adsorbing atom, the NO adsorption gives rise to IR bands with different frequencies thus enabling one to distinguish between the nature of the different types of adsorbent atoms on the surface. This feature is particularly important in the studies of the promoted Co-Mo and Ni-Mo catalysts since in contrast to previous studies using for example O₂ chemisorption, one may obtain simultaneous information about the adsorption occurring on the promoter atoms and on the Mo atoms. Thus, further insight into the structure of such catalysts can be obtained. Further-

more. from a comparison of the infrared/volumetric chemisorption results with HDS activity data, the origin of the promotion and the nature of the active sites in such catalysts can be elucidated. These different subjects will be discussed further below.

A. Structure of Sulfided Catalysts

a. *Co/Al₂O₃*. The adsorption of NO on both Co/Al₂O₃ catalysts with low Co loading (Figs. 2b and c) gives rise to two distinct bands but with different intensities indicating a variation in the concentration of surface Co atoms adsorbing NO.

For low loading catalysts, the major changes occurring upon sulfiding appear to be a partial or complete replacement of the oxygen atoms coordinated to the surface Co atoms by sulfurs (as indicated in the downward frequency shift in Fig. 2b as compared to Fig. 2a). Upon increasing the calcination temperature, Co has been observed to diffuse from octahedral positions at the surface to tetrahedral positions inside the alumina lattice resulting in less NO adsorbed on the calcined catalyst (17). Figure 2d shows that increasing the calcination temperature also results in a decrease in the amount of NO being adsorbed after sulfiding. Thus, the sulfiding treatment used presently seems only to affect the Co atoms located at the surface of the alumina and not those located in tetrahedral coordination in the subsurface layer of the alumina.

For the high loading Co/Al₂O₃ catalyst (Fig. 2e), the type of adsorption is quite different from that observed for the low loading catalysts and it is taken as typical for NO adsorbed on Co₉S₈. This indicates that the Co₃O₄ present on the surface of the calcined state (19) is readily transformed into Co₉S₈ upon sulfiding.

It is interesting that although the 6.5% Co/Al₂O₃ catalyst contains more than three times as much Co as the 2% Co/Al₂O₃ catalyst, the total amount of NO adsorbed is less (Fig. 3b). This decrease in NO adsorption is related to the fact that above a certain Co concentration, the formation of

bulk Co₃O₄ is favored over the formation of Co atoms at the surface of the alumina (17, 19).

b. *Mo/Al₂O₃*. The results of the chemisorption of NO on a reduced Mo/Al₂O₃ catalyst (Fig. 1b) are in good agreement with those of many previous authors (22–28) and the downward shift in the NO band frequency observed upon sulfiding (compare Figs. 1b and c) is similar to those reported recently by Okamoto *et al.* (28). However, the amount of NO adsorbed in the present study (expressed as NO/Mo) is somewhat larger than the values found by Okamoto *et al.* (28). This difference could be due to the fact that these authors used a static type of sulfiding procedure which also gave rise to quite low S/Mo values. The NO/Mo values observed presently are quite close to those observed by Jung *et al.* (29).

Okamoto *et al.* (28) have proposed that the adsorption of NO on sulfided Mo/Al₂O₃ catalysts occurs on tetrahedrally coordinated Mo species related to tetrahedral Mo species present in the calcined catalysts except for some exchange of oxygen with sulfurs. In other words, they proposed that the structure of the sulfided catalysts is quite similar to the oxysulfide structure envisioned in the monolayer model. We would like to propose a different NO adsorption site as discussed in the following.

Recently, it has been possible to obtain *in situ* structural information on Mo/Al₂O₃ catalysts using EXAFS (32). No evidence for oxysulfides was found in these studies for the 8.6% Mo/Al₂O₃ catalyst studied here (sulfided under similar conditions). Rather, Mo is predominantly present as MoS₂-like domains. Therefore, it seems likely that the adsorption of NO occurs mainly on Mo atoms present as MoS₂. The most probable adsorption sites are Mo atoms located at the edges of MoS₂ where the formation of CUS is favored. Thus, the NO adsorption is likely to be related to the edge dispersion of MoS₂. Adsorption of other molecules such as O₂ has in fact been observed to occur at the edges (37, 38).

The fact that MoS₂-like structures are

present in supported Mo catalysts readily explains the similar type of chemisorption and activity correlation between supported $\text{Mo}/\text{Al}_2\text{O}_3$ (2) and unsupported MoS_2 catalysts (7).

c. $\text{Co-Mo}/\text{Al}_2\text{O}_3$. From a comparison of Figs. 4e and d, it is evident that the NO adsorption on the $\text{Co-Mo}/\text{Al}_2\text{O}_3$ catalyst is quite different from that expected from a simple superposition of the individual component spectra (Fig. 4d). For example, the spectrum of the catalyst shows less NO adsorption on Mo atoms but more adsorption on Co atoms than expected from the behavior of the individual catalysts. This result and the nature of the changes in relative band intensity as discussed above indicate some type of interaction between Co and Mo atoms. This would seem to be in accord with the previous Mössbauer emission spectroscopy (MES) studies (13) of the same catalysts which show the presence of the so-called Co-Mo-S structure. In fact, the present results show (Fig. 12b) that there is a quite good correlation between the absorbance of the Co NO bands and the amount of Co atoms present as Co-Mo-S. (The catalysts with the largest absorbance deviate from a linear correlation. These are the catalysts which contain significant amounts of Co_9S_8 (13) which also adsorbs NO.) Therefore, it is likely that the Co atoms chemisorbing NO are predominantly those present as Co-Mo-S. It could be added that the present results also show that Co atoms occupy surface positions in Co-Mo-S.

In view of the catalytic importance of the Co-Mo-S structure, much effort has recently been directed toward establishing the positions of the Co atoms in this MoS_2 -like structure (10, 11). Although much of the recent evidence suggests that the Co atoms are located at MoS_2 edge positions, it has not been possible to establish this firmly (for a discussion see Ref. (14)). The present infrared results provide further support of this Co position. For the $\text{Co-Mo}/\text{Al}_2\text{O}_3$ catalysts with different Co/Mo ratios (but the

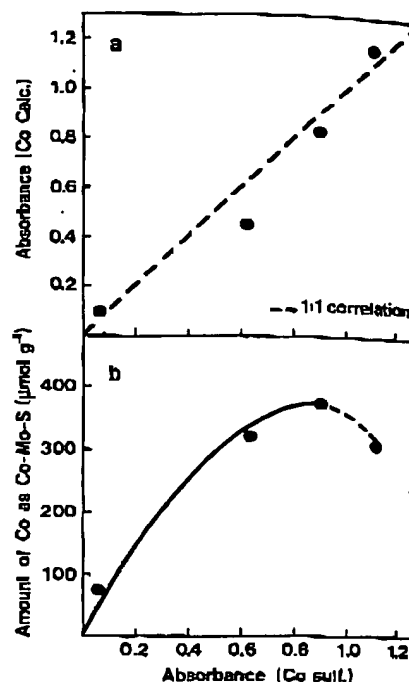


FIG. 12. The dependence of the absorbances of the ir bands of NO adsorbed on Co (1850 cm^{-1}) of sulfided $\text{Co-Mo}/\text{Al}_2\text{O}_3$ catalysts with different Co loading on different parameters. (a) The absorbances of the ir bands of NO adsorbed on Co (1885 cm^{-1}) of the corresponding calcined $\text{Co-Mo}/\text{Al}_2\text{O}_3$ catalysts and (b) the amount of Co in the form of Co-Mo-S (as determined by MES in (13)).

same Mo content), an increase in the intensity of the bands associated with NO adsorption on Co atoms is seen upon increasing the Co concentration. However, at the same time this is seen to give rise to a decrease in the intensity of the bands associated with adsorption on Mo atoms. For the $\text{Mo}/\text{Al}_2\text{O}_3$ catalysts, the adsorption of NO probably occurs, as discussed above, at the edges of the MoS_2 -like domains. EXAFS (32), as well as O_2 chemisorption results (8) indicate that the present catalysts all have about the same edge dispersion. Therefore, the decrease in the intensity of the Mo bands is taken as evidence for that Co is associated with the edges or corners of the MoS_2 structure, thereby occupying or covering some of the original

Mo sites. In other words, one may regard the Co-Mo-S "phase" identified in earlier MES studies (10, 11) as a MoS₂ phase with Co located (probably in atomic dispersion) along the edges at, for example, edge substitutional or interstitial positions. In many ways, the MoS₂ may be considered as the support for the Co atoms and the maximum amount of Co which can be present as Co-Mo-S will be expected to depend on the edge dispersion of the MoS₂. It is, however, seen that even for catalyst containing large amounts of Co, some Mo sites are still available for NO adsorption. This may indicate that Co has preference for certain sites such that a full edge coverage cannot be achieved.

The results on the effects of changing the calcination temperature (Figs. 5 and 6a) are also in accord with the above picture of the location of the Co atoms. In a previous study (17), it was found that increasing the calcination temperature resulted in less Co being present as Co-Mo-S after sulfiding. In agreement with this, Figs. 5 and 6 show that increasing the calcination temperature leads to a decrease in the number of Co atoms adsorbing NO after sulfiding. It is further seen that more Mo atoms are now available for the adsorption of NO (Fig. 6a) which agrees with less Co occupying the edges of the MoS₂.

d. Ni-Mo/Al₂O₃. The ir results for the Ni-Mo/Al₂O₃ catalysts show (see Fig. 11), very similar to the behavior for the Co-Mo/Al₂O₃ catalyst, that upon increasing the Ni content, the number of Ni atoms adsorbing NO increases, whereas the number of Mo atoms adsorbing NO decreases. This close analogy in the behavior of the Co-Mo and Ni-Mo catalysts indicates that the Ni-Mo catalysts also have the promoter atoms located at the edge positions of MoS₂. The downward shifts of the Ni band in the Ni-Mo/Al₂O₃ catalysts, in contrast to catalysts containing Ni only, reflects the interaction of Ni with Mo which apparently changes the electronic environment of Ni. The similar Mo band positions for Ni-Mo/Al₂O₃ and

Mo/Al₂O₃ catalysts indicate that the surface Mo atoms adsorbing NO have not been much affected by the promotion. The results on the Ni-Mo catalysts provide further evidence for that the Co-Mo-S type structure may be a general structural feature in promoted Mo (and W) based sulfide catalysts.

B. Relationship with Structures Present Prior to Sulfiding

The results on the Co/Al₂O₃ catalysts show that the structure of the sulfided catalysts to a large extent is predetermined by the type of phases present in the calcined state. This is apparently related to the fact that each of the phases observed in the calcined catalysts responds in a certain way to the sulfiding treatment. This has also been observed previously (17, 21) for Co-Mo/Al₂O₃ catalysts where it was shown that the Co-Mo-S structure seemed to be formed from the octahedrally coordinated Co present at the surface of the alumina. The results shown in Fig. 12a, where a correlation between the Co atoms adsorbing NO in the calcined state and those adsorbing NO in the sulfided state is observed, give further evidence for such a relationship. Moreover, an increase in the calcination temperature, which causes Co to diffuse into the alumina (17, 19), leads to less Co adsorbing NO (and present as Co-Mo-S) in the sulfided state. This also shows the close relationship between the structure of the precursor and that of the sulfided catalyst. The behavior of Ni-Mo/Al₂O₃ catalysts is found to be rather similar to that of the Co-Mo system (39).

C. Catalytic Implications

It is quite clear from a comparison of Figs. 7a and c and from Fig. 8c that no simple correlation exists between the total amount of NO chemisorbed on the Co-Mo catalysts and HDS activity of these catalysts. It is seen that while the HDS activity

changes by a factor of more than 10, the total NO uptake only varies by a factor of less than 3. Furthermore, it is observed that catalysts with very low activity may have large NO uptakes and also the catalysts with the largest NO chemisorption are not those with maximum activity. It may be worth noting that for the present catalysts, no simple correlation was observed with total O_2 chemisorption either (8). Nevertheless, despite the absence of a direct correlation between the catalytic activity and the total amount of NO chemisorbed, NO chemisorption may, if combined with the infrared spectroscopic results, provide useful clues to the nature of the active sites and the promotion of the HDS activity in such catalysts.

The infrared results allow one to separate the contributions from NO adsorption on the Mo atoms from that on the promoter atoms. For Co-Mo/ Al_2O_3 catalysts calcined at different temperatures (Fig. 6), and Co-Mo/ Al_2O_3 (or Ni-Mo/ Al_2O_3) catalysts containing different concentrations of Co (or Ni) promoter atoms (Figs. 7, 8, and 11), a correlation is found between the increase in the HDS activity of these catalysts and the absorbance of the Co (or Ni) bands. However, for all these catalysts, no correlation is apparent between the activity and the amount of NO adsorbed on the Mo atoms. In fact, the catalysts with the highest activity are those with the fewest Mo atoms adsorbing NO. This latter result clearly demonstrates that the role of the promoter atoms is not to create more of the type of sites present in the unpromoted Mo/ Al_2O_3 catalysts. Instead, the primary role of the promoter atoms is to create a new more active type of sites associated with the promoter atoms in the Co-Mo-S or Ni-Mo-S structures. In general, one will expect contributions to the HDS activity from both promoted and unpromoted sites but it is seen that even in the case of minor concentrations of promoted sites these will dominate the HDS activity for Co-Mo and Ni-Mo catalysts. The present results are in

agreement with previous Mössbauer emission spectroscopy measurements (13-18) where the HDS activity was shown to be related to the amount of Co present in the form of Co-Mo-S. The ir results extend the conclusions to Ni-Mo catalysts and it is likely that other promoted HDS catalysts will show many similarities.

In the case of the Co-Mo/ Al_2O_3 catalysts with different Co-Mo atomic ratios (and constant Mo content), the catalytic activity was proportional to the absorbance of NO on Co atoms for low Co/Mo ratios. However, for high Co/Mo ratios, some deviation from linearity is observed (Fig. 8a). This deviation is probably due to formation of bulk Co_9S_8 (13) which also adsorbs NO. Nevertheless, one may estimate the amount of Co present as Co-Mo-S by calculating the decrease in absorbance of Mo bands due to the presence of different amounts of Co, which in view of the above results, reflects the fraction of Mo edge sites covered by Co atoms. Indeed, when the catalytic activity is plotted against this parameter (Fig. 13), a remarkably good linear relationship is observed even for the catalysts which contain Co_9S_8 . The existence of such a correlation supports both the structural description of these catalysts and the catalytic significance of the different sites present. It should perhaps be added that the above results also indicate

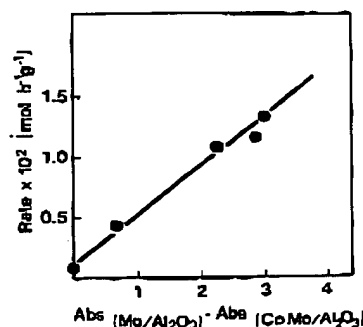


FIG. 13. Thiophene HDS activities as function of the difference in absorbance of the ir bands of NO adsorbed on Mo between the unpromoted and the different promoted catalysts.

that in the present catalysts, Co₉S₈ does not contribute significantly to the overall catalytic activity.

It is known that pyridine is a poison for the HDS activity for both Mo/Al₂O₃ and Co-Mo/Al₂O₃ catalysts (33–35). The present result (Fig. 9) shows that preadsorption of pyridine leads to a drastic decrease in the absorption bands associated with both Co and Mo atoms. Thus, for the present catalysts both the more active promoted and the less active unpromoted sites are poisoned. It is seen from Fig. 9 that some NO adsorption on sites associated with Co still occurs which is in agreement with the observation that the HDS activity is not completely poisoned by adsorption of pyridine (35).

In past studies, no clear correlation was found between the HDS activity and the chemisorption of other probe molecules such as O₂ on promoted catalyst (3–9). In view of the present results, this situation is probably due to the fact that these molecules may titrate both the more active promoted sites and the less active unpromoted sites along the edges of the MoS₂-like structures. Therefore, the type of correlation observed will be expected to depend on the extent that the probe molecules have preferentially titrated the more active promoted sites associated with the Co or Ni (present as Co-Mo-S or Ni-Mo-S).

The fact that the activity for the different catalysts is found to be proportional to the number of Co (Ni) atoms at the edges of MoS₂ indicates that the new high activity sites are associated with the promoter atoms. However, these results do not allow one to conclude whether these sites are associated solely with the promoter atoms or if the surrounding Mo atoms also play a vital role, for example, by modifying the redox properties or by changing the bond strength of the sulfur atoms (for a discussion of some of the different possibilities see Ref. (40)). More research is obviously needed before a detailed understanding can be achieved on how the presence of the

promoter atoms along the edges of the MoS₂ structure can create sites with much higher intrinsic HDS activity.

V. CONCLUSION

The present study demonstrates that NO may be a useful selective probe molecule for elucidating the nature of the surface species present in sulfided HDS catalysts. The fact that the frequencies of the ir bands of the adsorbed NO are sensitive to the type of atoms and local environment makes it possible to acquire information on the promoter atoms (Co or Ni) and the Mo atoms simultaneously. This possibility is especially valuable in view of the fact that the HDS activity fails to show a simple correlation with the total NO adsorption but only with the fraction adsorbed on the promoter atoms. It is perhaps noteworthy that, in contrast to the present studies, the many O₂ chemisorption studies of promoted catalysts reported recently (3–9) could not discriminate between the adsorption occurring on the different atoms. Thus, no general valid correlations could be made between the O₂ chemisorption and the HDS activity.

It is presently found that the Co atoms, which adsorb NO and seem to be responsible for the promotion of the HDS activity, are related to the Co atoms which Mössbauer emission spectroscopy has shown (see, e.g. (10, 14, 40)) to be present in the so-called Co-Mo-S structure. Previous results have shown that Co-Mo-S has a MoS₂-like structure (see (10–12, 14, 40)). The present findings provide further details on the nature of these structures and indicate that the Co atoms are situated at edges or corner positions. Furthermore, it is shown that Ni-Mo catalysts behave analogously. The edge coverage by the promoter atoms causes a blocking of some of the Mo adsorption sites. Thus, besides being involved in the creation of new sites with high intrinsic HDS activity, the promoter atoms present at the MoS₂ edges will probably also give rise to a decrease in the concen-

tration of the less active unpromoted sites (i.e., those possessing the HDS activity in the unpromoted catalysts).

For both Co-Mo and Ni-Mo catalysts the intrinsic HDS activity of the promoted sites seems to be considerably greater than that of the unpromoted sites. Thus, even in the case of relative small concentrations of promoted sites, the HDS activity will be dominated by the reaction occurring on these sites. We are presently investigating the catalytic role of such promoted and unpromoted sites in other catalyst systems and for reactions other than HDS.

ACKNOWLEDGMENT

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REFERENCES

1. Tauster, S. J., Pecoraro, T. A., and Chianelli, R. R., *J. Catal.* **63**, 515 (1980).
2. Bachelier, J., Duchet, J. C., and Cornet, D., *Bull. Soc. Chim. Belg.* **90**, 1301 (1981).
3. Tauster, S. J., and Riley, J. L., *J. Catal.* **67**, 250 (1981).
4. Tauster, S. J., and Riley, J. L., *J. Catal.* **70**, 230 (1981).
5. Bodrero, T. A., Bartholomew, C. H., and Pratt, K. C., *J. Catal.* **78**, 253 (1982).
6. Zmicrzak, W., MuraliDhar, G., and Massoth, F. E., *J. Catal.* **77**, 432 (1982).
7. Burch, R., and Collins, A., in "Proceedings of the Climax Fourth International Conference on Chemistry and Uses of Molybdenum" (H. F. Barry and P. C. H. Mitchell, Eds.), p. 374. Climax Molybdenum Company, Ann Arbor, Michigan, 1982.
8. Topsøe, H., Bartholdy, J., Clausen, B. S., and Candia, R., paper presented at the ACS symposium on Structure and Activity of Sulfided Hydroprocessing Catalysts, Kansas City, 1982.
9. Bachelier, J., doctor thesis, University of Caen, 1982; Bachelier, J., private communications; Bachelier, J., Duchet, J. C., and Cornet, D., *J. Catal.* **76**, 300 (1982).
10. Clausen, B. S., Mørup, S., Topsøe, H., and Candia, R., *J. Phys. Colloq.* **37**, C6-287-290 (1976).
11. Topsøe, H., Clausen, B. S., Candia, R., Wivel, C., and Mørup, S., *J. Catal.* **68**, 433 (1981).
12. Clausen, B. S., Lengeler, B., Candia, R., Als-Nielsen, J., and Topsøe, H., *Bull. Soc. Chim. Belg.* **90**, 1249 (1981).
13. Wivel, C., Candia, R., Clausen, B. S., Mørup, S., and Topsøe, H., *J. Catal.* **68**, 453 (1981).
14. Topsøe, H., Clausen, B. S., Candia, R., Wivel, C., and Mørup, S., *Bull. Soc. Chim. Belg.* **90**, 1189 (1981).
15. Candia, R., Clausen, B. S., and Topsøe, H., *Bull. Soc. Chim. Belg.* **90**, 1225 (1981).
16. Breysse, M., Bennett, B. A., Chadwick, D., and Vrinat, M., *Bull. Soc. Chim. Belg.* **90**, 1271 (1981).
17. Candia, R., Topsøe, N.-Y., Clausen, B. S., Wivel, C., Nevald, R., Mørup, S., and Topsøe, H., in "Proceedings of the Climax Fourth International Conference on Chemistry and Uses of Molybdenum" (H. F. Barry and P. C. H. Mitchell, Eds.), p. 374. Climax Molybdenum Company, Ann Arbor, Michigan, 1982. Wivel, C., Clausen, B. S., Mørup, S., Candia, R., and Topsøe, H., submitted for publication.
18. Candia, R., Clausen, B. S., and Topsøe, H., *J. Catal.* **77**, 564 (1982).
19. Topsøe, N.-Y., and Topsøe, H., *J. Catal.* **75**, 354 (1982).
20. Topsøe, N.-Y., and Topsøe, H., *Bull. Soc. Chim. Belg.* **90**, 1311 (1981).
21. Topsøe, N.-Y., and Topsøe, H., *J. Catal.* **77**, 295 (1982).
22. Millman, W. S., and Hall, W. K., *J. Phys. Chem.* **83**, 427 (1979).
23. Millman, W. S., and Hall, W. K., *J. Catal.* **59**, 311 (1979).
24. Yao, H. C., *J. Catal.* **70**, 440 (1981).
25. Yao, H. C., and Rothschild, W. G., in "Proceedings of the Climax Fourth International Conference on Chemistry and Uses of Molybdenum" (H. F. Barry and P. C. H. Mitchell, Eds.), p. 31. Climax Molybdenum Company, Ann Arbor, Michigan, 1982.
26. Peri, J. B., *J. Phys. Chem.* **86**, 1615 (1982).
27. Segawa, K.-I., and Hall, W. K., *J. Catal.* **77**, 221 (1982).
28. Okamoto, Y., Katoh, Y., Mori, Y., Imanaka, T., and Teranishi, S., *J. Catal.* **70**, 445 (1981).
29. Jung, H. J., Schmitt, J. L., and Ando, H., in "Proceedings of the Climax Fourth International Conference on Chemistry and Uses of Molybdenum" (H. F. Barry and P. C. H. Mitchell, Eds.), p. 246. Climax Molybdenum Company, Ann Arbor, Michigan, 1982.
30. Turnham, B., Ph.D. dissertation, Stanford University, 1975.
31. Howe, R., and Kemball, C., *J. Chem. Soc. Faraday Trans. 1* **70**, 1153 (1974).
32. Clausen, B. S., Topsøe, H., Candia, R., Villedisen, J., Lengeler, B., Als-Nielsen, J., and Christensen, F., *J. Phys. Chem.* **85**, 3868 (1981).
33. Cowley, S. W., and Massoth, F. E., *J. Catal.* **51**, 291 (1978).

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34. Desikan, P., and Amberg, C. H., *Canad. J. Chem.* 42, 843 (1964).
35. Ramachandran, R., and Massoth, F. E., *Chem. Eng. Commun.* 18, 239 (1982).
36. Morrow, B. A., and Moran, L. E., *J. Catal.* 62, 294 (1980).
37. Bahl, F. O., Evans, E. L., and Thomas, J. M., *Proc. Roy. Soc. A* 306, 53 (1968).
38. Salmeron, M., Somorjai, G. A., Wold, A., Chianelli, R. R., and Liang, K. S., *Chem. Phys. Lett.* 90, 105 (1982).
39. Topsøe, N.-Y., and Topsøe, H., unpublished results.
40. Topsøe, H., in "Surface Properties and Catalysis by Non-Metals: Oxides, Sulfides and other Transition Metal Compounds," p. 326. Reidel, Dordrecht, 1983.